Inorganica Chimica Acta, 80 (1983) L65–L67

Synthesis and Selected Properties of a Reduced Single-Cubane Cluster Containing the $[MoFe_3S_4]^{2+}$ (S = 2) Core

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Received June 9, 1983

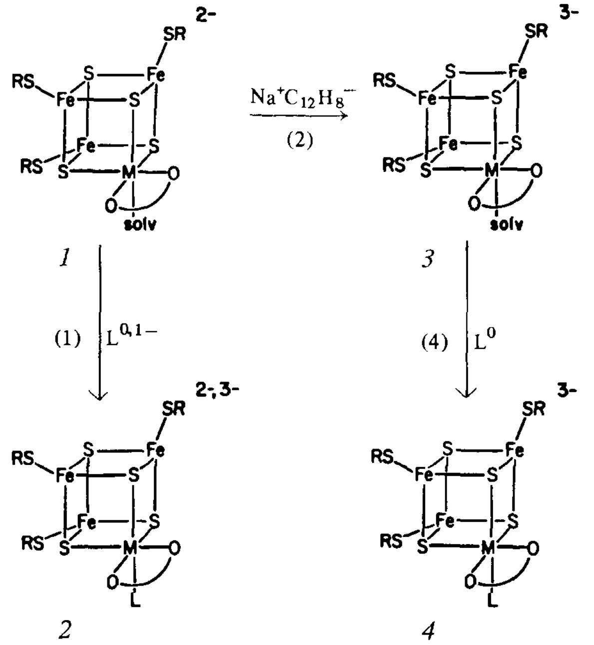
In our ongoing investigations of M–Fe–S clusters (M = Mo, W), many aspects of which have been summarized [1, 2], a synthetic route to the solvated single-cubanes *1* in solution has been developed [3]. These species may be converted to the M–ligated forms *2* (L = RO^-, RS^-, CN^-, PR_3) by the stoichiometric reaction 1 in acetonitrile [3–6]. Proof of the single-cubane nature of these clusters has been provided by X-ray structural determinations of compounds containing $[MoFe_3S_4Cl_3(al_2cat)(THF)]^{2-}$ [6] (*1*, chloride in place of thiolate, al_2cat = 3,6-diallylcatecholate dianion) and $[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_4(al_2cat)]^{3-}$ [4, 5] (*2*, L = $p\text{-}ClC_6H_4S$). Cluster types *1* and *2* contain the $\alpha = [MoFe_3S_4]^{3+}$ core with electronic and Mo–site structural properties that resemble those of the FeMo–cofactor (FeMo–co) of nitrogenase [1–7]. The solvated clusters *1* were designed to provide a labile coordination site for the purpose of binding enzymic and other substrates potentially subject to reductive transformations. Any such transformation would doubtless implicate reduced clusters with the $\beta = [MoFe_3S_4]^{2+}$ core, of which solvated *3* is an obvious precursor to reduced substrate-bound clusters. The conversion *1* → *3* has been achieved *in situ* by use of sodium acenaphthylenide, reaction 2 [5], but the reduced clusters *3* were not isolated.

Here we describe the synthesis and isolation of a prototypic cluster *3* by this reaction and certain of its properties.

Experimental

Preparation of $(Et_4N)_3[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_3(al_2cat)(EtCN)]$

All operations were carried out under a pure argon atmosphere. Propionitrile, *n*-hexane, and THF were freshly distilled from CaH_2 prior to use. A ~0.4 *M* solution of sodium acenaphthylenide was prepared by the addition of 44 mg (1.9 mmol) of sodium in very small pieces to a solution of 286 mg (1.88 mmol) of sublimed acenaphthylene in 4.4 ml of THF. The deep brown mixture was stirred overnight before use. A suspension of 800 mg (0.315 mmol) of $(Et_4N)_4[Mo_2Fe_6S_8(S\text{-}p\text{-}C_6H_4Cl)_6(al_2cat)_2]$ [3] and 132 mg (0.628 mmol) of dry Et_4NBr in 12 ml of propionitrile was prepared. To the stirred suspension 1.85 ml (0.790 mmol) of sodium acenaphthylenide in THF was added slowly. The initial red-brown color of the suspension changed to greenish-brown and soon thereafter a nearly homogeneous solution formed. After being stirred for 30 min the solution was filtered. *n*-Hexane (30 ml) was carefully layered over the filtrate and the mixture was allowed to stand undisturbed for 5 days. During this time an oily material formed at the bottom of the flask and crystals deposited on the sides. The latter were collected by filtration, washed with 5 ml of n-hexane, and dried *in vacuo*; 420 mg (46%) of pure product was obtained as black crystals. Elemental analyses are consistent with a propionitrile solvate. *Anal.* Calcd. for $C_{57}H_{89}Cl_3Fe_3MoN_4S_7$: C, 48.06; H, 6.30; Fe, 11.76; Mo, 6.73; N, 3.93; S, 15.76. Found: C, 47.69; H, 6.12; Fe, 11.61; Mo, 6.53; N, 3.72; S, 15.36. Absorption spectrum (N,N-dimethylacetamide (DMA)): λ_{max} 308 (ϵ_M 31,400), 362 (26,000), 415(sh) nm. Upon drying *in vacuo* the oily residue converted to a gummy solid (~200 mg) which gave the same ^1H NMR spectrum as the crystalline material. The product is extremely sensitive to oxidation, especially in solution.



Results and Discussion

$(Et_4N)_3[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_3(al_2cat)(EtCN)]$ is the first single-cubane compound isolated in the β

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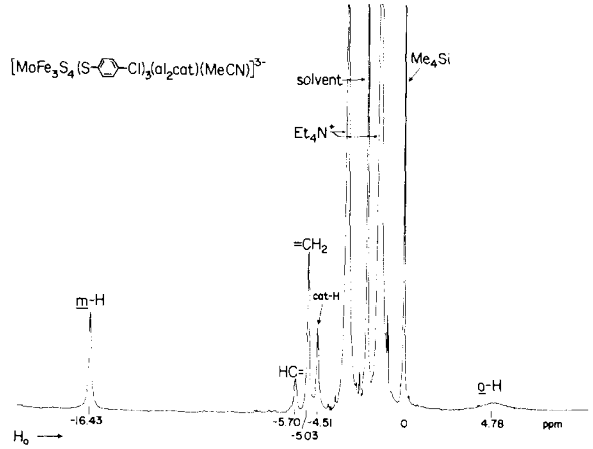

Fig. 1. ^{1}H NMR spectrum (300 MHz) of $(Et_4N)_3[MoFe_3S_4(S{-}p{-}C_6H_4Cl)_3(al_2cat)(MeCN)]^{3-}$ in CD_3CN solution at ~297 K; signal assignments are indicated.

oxidation level. Diffraction quality crystals have not been obtained; core dimensions are presumably similar to those of the reduced double-cubane $[Mo_2Fe_6S_8(\mu\text{-}SPh)_3(SPh)_6]^{5-}$ (2 β units) whose structure has been determined as its Et_4N^+ salt [8]. The ^{1}H NMR spectrum of the solvate cluster in CD_3CN solution, shown in Fig. 1, contains several noteworthy features. Compared to the analogous oxidized cluster *1* [5], isotropic shifts of *o*-H and *m*-H are of the same sign but larger and the catecholate (cat–H) signal is displaced to high field (–4.51 ppm). In the oxidized cluster this resonance is shifted to low field (–9.35 ppm). The single set of R = p-C_6H_4Cl signals indicates that, as for all solvated clusters *1* [3, 5, 6], the static C_s symmetry of *3* is averaged to effective trigonal symmetry by rapid binding and dissociation of solvent molecules and attendant degenerate reorientations of the catecholate ring. This process is set out in detail elsewhere [6]. The spectrum of the isolated cluster is essentially the same as that reported for the species generated by reaction 1 [5], thereby validating that procedure. Other properties of isolated $[MoFe_3S_4(S{-}p{-}C_6H_4Cl)_3(al_2cat)(EtCN)]^{3-}$ [7] include a reversible 2–/3– electron-transfer reaction with $E_{1/2}$ = –1.09 V (DMF), a spin-quintet ground state, established by low temperature magnetization measurements and consistent with the value of $5.12\mu_B$ at 297 K, and ^{57}Fe isomer shifts δ = 0.40 and 0.42 mm/s (4.2 K, *vs.* Fe metal) indicative of substantial Fe(II) character of the core. Thus in the redox step 2–(α) → 3–(β) the spin change $S = 3/2 \rightarrow 2$ occurs and δ values increase to an extent that, from the linear correlation of δ and (mean) oxidation state [8], the Fe_3 portion and associated sulfur atoms of the core are those primarily affected by reduction. Inasmuch as these effects are also found in the double-cubane series $[Mo_2Fe_6S_8(SPh)_9]^{3-,4-,5-}$ [8], they are likely of general occurrence in $\alpha \rightleftarrows \beta$ oxidation level changes.

Recently we have shown that $[Mo_2Fe_6S_8(SPh)_9]^{5-}$ in DMA solution is oxidized to the 3– cluster by a large excess of PhSH and by 2 equiv of $(Et_3NH)(PF_6)$ with formation of 1.0 and 0.83 mol H_2/mol cluster, respectively [9]. A similar reaction system containing the reduced single-cubane and excess p-ClC_6H_4SH gave negligible H_2 and $[Mo_2Fe_6S_8(S{-}p{-}C_6H_4Cl)_9]^{3-}$, identified by ^{1}H NMR comparison with an authentic sample [10], as the main cluster product. However, the system in reaction 3 (2 m*M* cluster) gave a 36% H_2 yield* after

$$2[MoFe_3S_4(S{-}p{-}C_6H_4Cl)_3(al_2cat)(DMA)]^{3-} + 2(Et_3NH)(PF_6) \xrightarrow{DMA} 2[MoFe_3S_4(S{-}p{-}C_6H_4Cl)_3(al_2cat)(DMA)]^{2-} + H_2 + Et_3N + PF_6^- \qquad (3)$$

20 hr. Use of the previously demonstrated reaction 4 [5], here with L = ½ $Me_2PCH_2CH_2PMe_2$(dmpe), resulted in the formation of the linked, reduced double-cubane 4·(dmpe)·4. The ^{1}H NMR spectrum (–19.9(1), –14.5(2), *m*-H; –11.1 (~1), cat-H, ppm in CD_3CN) is consistent with cluster C_s symmetry, as found with *4* (L = PEt_3) [5]. Reaction of 2 mols of Et_3NH^+/mol 4·(dmpe)·4 (1 m*M*) in DMA afforded a 61% H_2 yield after 20 hr. In both systems formation of *1* or *2* as the only oxidized cluster product in detectable amounts was established by a combination of ^{1}H NMR, uv-visible spectral, and voltammetric observations. The probable advantage of a two-electron carrier in effecting H_2 evolution from protic sources has been considered [9]. The present results, together with those for $[Mo_2Fe_6S_8(SPh)_9]^{5-}$ [9], demonstrate that a labile binding site on a $MoFe_3S_4$-type cluster prior to incubation with a protic source is not a requirement for H_2 formation. Yields of H_2 are modest** compared to those in the $[Mo_2Fe_6S_8(SPh)_9]^{5-}$/PhSH, Et_3NH^+ systems, but do indicate the ability of reduced clusters to effect reduction of at least one nitrogenase substrate (H^+). Reduction of other substrates (*e.g.*, acetylenes, N_3^-, N_2) is very likely to require a labile site. This matter is being pursued in studies of reactions of solvated clusters *1* and *3* in media of different coordinating strengths. Although these clusters do not conform to the composition of FeMo–co (6–8Fe:~9S:Mo [11–13]), they are the best molecules currently available for examining reactivity at a Mo site structurally similar to that in the cofactor.

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*H_2 was detected as in ref. 9.

**H_2 yields are dependent on solvent purity [9]; those determined here are not necessarily maximal.

Acknowledgements

This research was supported by National Science Foundation Grant 81-06017. We thank Dr. T. Yamamura for experimental assistance and useful discussions.

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